Mössbauer Isomer Shift in Gold Microcrystals*

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The Mössbauer isomer shift of Au^{197} has been measured in samples of gold microcrystals supported in gelatin. The experimental isomer shift can be correlated with the lattice contractions observed in these microcrystals.

I. INTRODUCTION

Major modifications of the crystal lattice may occur in microcrystals with diameters on the order of 100 Å and less. A variety of these lattice modifications have been studied by means of the Mössbauer effect (ME) (see Ref. 1 for a recent review of such effects). The ME is particularly suitable for microcrystal studies because it directly samples the microscopic surroundings of the emitting or absorbing nucleus. This is in contrast to other techniques which are dependent on gross effects, such as x-ray scattering with its broadening in microcrystals due to incoherence effects, or resistivity measurements which are hampered by the many interfaces in microcrystal samples.

One of the lattice modifications which has frequently been observed in microcrystals (see Refs. 2–6, for example) is a change in the lattice spacing, resembling a pressure effect. One of the ME parameters which might therefore be expected to vary with particle size is the isomer shift, as this is dependent on electron densities which are sensitive to pressure.

Gold is one metal in which a lattice contraction has been previously observed in microcrystals.[2–4] It is also a material in which the ME isomer shift as a function of pressure has been measured and theoretically interpreted.[7,8] One might therefore expect to see some Mössbauer isomer shifts in gold microcrystals, and to be able to relate them to such lattice distortions.

In this paper we report on experiments with gold microcrystals in which both the ME isomer shifts and the lattice modifications were measured for two different samples. The measured values of the isomer shifts are then compared with the values predicted on the basis of the changes in electron density at the nucleus due to the measured lattice contractions.

II. EXPERIMENTAL DETAILS AND RESULTS

A. Preparation of Gold Microcrystals

The gold microcrystals were prepared following the procedure of Wilenzick *et al.*[9] This involved the following steps: (1) First a hydrosol of gold was formed in water by reducing a gold chloride solution with sodium citrate. This led to a colloidal dispersion of small gold crystallites through a condensation or precipitation process. (2) Then the excess reducing agent was removed by dialysis for 2 to 5 days in 1/2-in. cellulose tubing. (3) Small amounts of gelatin were then added, which formed the matrix to protect the hydrosol in the subsequent dehydration process. (4) Finally the very dilute gold microcrystal solution was heated at about 75°C under the partial vacuum of an aspirator and thus concentrated. Typical final concentrations of the samples were 20 mg of Au per cm^3.

Two different samples containing microcrystals whose diameters are nominally 60 Å were prepared in this way. These we shall refer to as samples I and II. The difference between these two samples involved somewhat different glassware-cleaning procedures, slightly different gelatin concentrations, slight variations in the dehydration procedure, and perhaps "artistic" differences between the two persons preparing the samples.

B. Measurements of Microcrystal Sizes and Lattice Contractions

For these two samples we measured both the microcrystallite size and the lattice contractions which occur in them (compared to bulk) by means of a Phillips x-ray goniometer. In these measurements the $K\alpha$ x rays emitted by a Cu target were scattered from the surface of the microcrystal samples, and the count rate as a function of the scattering angle 2θ was recorded as a pen tracing in a chart recorder. Figure 1 shows such a count rate record for several angular regions both for bulk and for microcrystal sample II. The microcrystal-sample trace differs from that for the bulk, both with respect to the peak width and the angular position of the Bragg peaks. The average particle size can be extracted from the width of the peak, and the average lattice contraction from the peak position compared to that of the analogous bulk-gold peak.

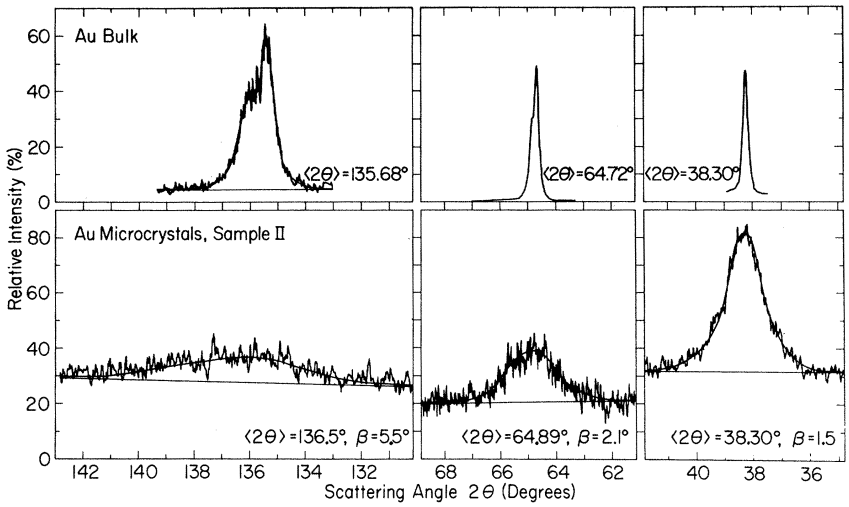

FIG. 1. X-ray spectra of bulk and microcrystal gold samples taken with Cu $K\alpha$ x rays. The x-ray count rate is plotted as a function of the scattering angle 2θ, where $\theta=90°$ corresponds to perpendicular incidecne of the x rays onto the sample.

Owing to the limited number of scattering planes (and their finite area) involved in any one Bragg reflection in microcrystals, there is a resultant broadening in the diffraction peaks. The equation relating the peak breadth β, and the particle size D, is[10]

$$D=K\lambda/\beta\cos\theta, \tag{1}$$

where λ is the wave length of the scattered radiation (1.542 Å for the Cu $K\alpha$ x rays), and θ is the Bragg scattering angle. The value of K depends on the definitions of D and β, the shape of the crystallites, and the indices of the reflecting planes. In evaluating our data, we took $K=1.107$, with β being defined as the peak width at half maximum of the Bragg peak in terms of 2θ, and D being the crystallite diameter. This value of K holds for all reflecting planes in the case of spherical crystallites. A correction for the instrumental broadening was included in the evaluation, but this modified the obtained particle size only a little. The linewidths and particle sizes obtained for the two samples are shown in Table I. The average particle sizes determined in this way are $D=62\pm12$ Å and 67 ± 12 Å for samples I and II, respectively.

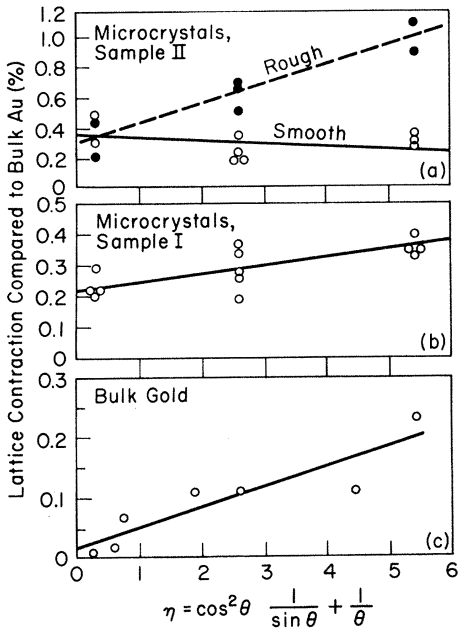

FIG. 2. Lattice distortions of various gold samples measured by Bragg reflection of x rays. The straight-line fits of the data allow extrapolations to $\theta=90°$ (perpendicular incidence of the x rays).

In Fig. 1 there is clearly visible a shift in the peak positions from the bulk to the microcrystals. The Bragg equation relating the lattice spacing and the angular position of the peak is[10]

$$\lambda=2d(\sin\theta)/n(h^2+k^2+l^2)^{1/2}, \tag{2}$$

where $d/n(h^2+k^2+l^2)^{1/2}$ is the equivalent lattice spacing for nth order scattering from a given hkl lattice plane, λ is the wavelength of the scattered radiation, and θ is the Bragg angle. The deviation $\Delta d/d$ in these equivalent spacings from the bulk values are then related through

$$\Delta d/d=-\cot\theta\Delta\theta=\Delta a/a_0, \tag{3}$$

where a_0 is the spacing between unit cells in the bulk lattice. In determining $\Delta a/a_0$ for the samples, corrections may have to be applied for the physical sample configuration. Our samples are made up mainly of gelatin and therefore it is difficult to prepare a sample with a flat surface. This can lead to erroneous values for the lattice spacing, particularly for low-angle Bragg peaks. To eliminate this source of error it is customary[10] to use some technique involving extrapolation to $\theta=90°$ (i.e., perpendicular incidence of the x rays on the sample). A parameter, which takes into account several

TABLE I. Lattice contraction and particle size for gold microcrystal samples I and II (the latter once for a coarse sample surface and once for a smoother sample surface). The data were obtained with a Phillips x-ray goniometer using Cu $K\alpha$ x rays.

Sample	2θ (nominal)	$\Delta 2\theta$ (deg)	$\Delta a/a_0$ (%)	$\beta_{1/2}$ (deg)	Diameter (Å)
I	38.21	+0.16	−0.40	1.35	77
		+0.14	−0.35	1.66	62
		+0.13	−0.33	1.72	60
		+0.14	−0.35	1.44	72
	64.63	+0.14	−0.19	1.87	62
		+0.19	−0.26	2.25	51
		+0.27	−0.37	1.80	64
		+0.20	−0.28	2.18	53
		+0.25	−0.34	1.98	58
	135.64	+0.55	−0.20	2.75	94
		+0.81	−0.29	5.2	50
		+0.61	−0.22	4.4	59
		+0.61	−0.22	6.8	38
	extrapolation		−0.22±0.06		62±12
II (coarser sample surface)	38.21	+0.36	−0.90	1.47	70
		+0.43	−1.09	1.48	70
	64.63	+0.37	−0.54	2.0	56
		+0.48	−0.66	2.08	54
		+0.49	−0.68	1.95	56
	135.64	+0.61	−0.22	6.7	37
		+1.26	−0.45	6.3	40
	extrapolation		−0.31		55
II (smoother sample surface)	38.21	+0.14	−0.35	1.36	76
		+0.11	−0.28	1.49	69
		+0.12	−0.30	1.42	73
	64.63	+0.14	−0.19	1.57	74
		+0.26	−0.36	1.62	71
		+0.14	−0.19	1.77	65
		+0.19	−0.25	1.62	71
	135.64	+0.86	−0.31	5.5	47
		+1.06	−0.48	3.9	66
	extrapolation		−0.37±0.09		67±12

of the possible sources of error in lattice-spacing determinations, is

$$\eta = (\cos^2\theta/\sin\theta) + (\cos^2\theta/\theta). \quad (4)$$

Plotting $\Delta a/a_0$ as a function of η, the deviations in $\Delta a/a_0$ due to sample configuration should go to zero as η goes to zero.

Figure 2 shows such plots for the two gold microcrystal samples and for bulk, together with straight-line fits for the extrapolation to $\eta=0$. For sample II, two different sets of data are shown; the data with the greater slope was taken with the sample surface being far less smooth than for the data set with the lesser slope. Since the extrapolation is more reliable for the data with the lesser slope, we have adopted the values $\Delta a/a_0 = (-0.22\pm0.06)\%$ and $(-0.37\pm0.09)\%$ for samples I and II, respectively.

These microcrystal Bragg peaks are quite broad, and are superimposed on an x-ray scattering background distribution whose angular dependence can only be estimated. The extreme dilution of the gold in the gelatin means that this background is quite significant compared to the peak size. The subtraction of this uncertain background sets an ultimate limit to the precision with which D and $\Delta a/a_0$ can be evaluated by this technique.

We have also examined these gold microcrystal

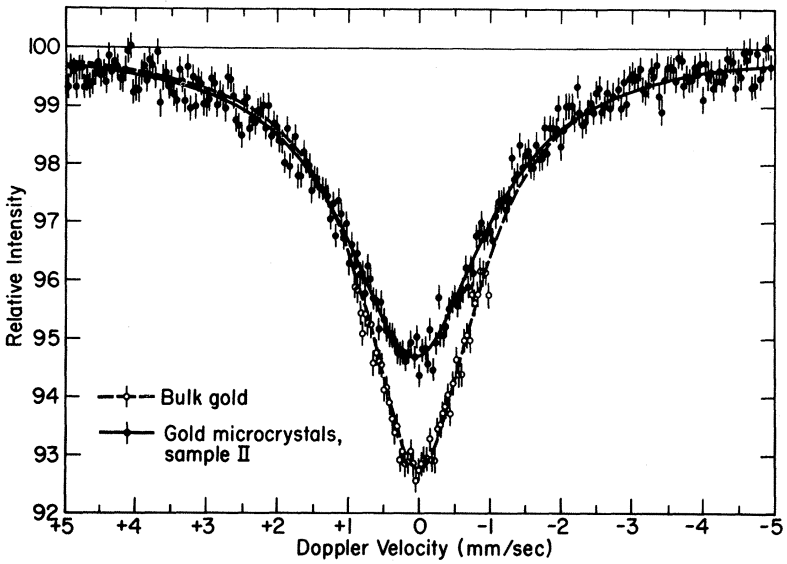

FIG. 3. Count rate as a function of the Doppler velocity for a source of Pt^{197} in platinum, and absorbers of bulk gold and gold microcrystal sample II. The center of the bulk-gold spectrum is defined as zero velocity, and a positive velocity corresponds to the source approaching the absorber.

samples with an electron microscope. With the available resolution we were able to set an upper limit of 150 Å to the size of the particles.

C. Mössbauer Isomer Shift Measurements

The Mössbauer isomer shift of the 77.3-keV state in Au^{197} for these two gold microcrystal samples, as well as for bulk gold, has been measured. The apparatus and procedure used have been described previously.[8] Both the source of Pt^{197} in a Pt foil and the microcrystal (or bulk) gold absorbers were cooled to liquid-helium temperatures for these experiments. The λ rays were detected with a Ge(Li) detector. The Mössbauer spectra were recorded simultaneously with a calibration spectrum of a Co^{57} in Cu source versus an Fe foil. This procedure yields an instrumental stability and precision in the Doppler velocity of about 10^{-3} mm/sec.

Figure 3 shows the ME resonance spectra obtained for microcrystal sample II as compared to bulk. The net isomer shifts relative to bulk determined from such spectra were $+0.034\pm0.012$ and $+0.089\pm0.026$ mm/sec for samples I and II, respectively. These positive isomer shifts mean that maximum resonance occurred when the source was moving toward the absorber; according to previous Mössbauer experiments[8] this indicates that the electron density at the nucleus is higher for these microcrystals than for bulk.

III. DISCUSSION

A. Particle Size versus Lattice Spacing

We now compare our data on the lattice contractions for our gold microcrystal samples both with theory and with the experimental data of other investigators.

It has been known for some time that the lattice in microcrystals is likely to be distorted as compared to bulk.[2–6,11–15] The presence of the large surface area in such microcrystals means that there will be a sizable fraction of the atoms in an asymmetric environment. Some of the bonds of these atoms will be modified. Therefore there will be a surface free energy which will be related to the surface tension in the liquid state. To first order the resulting lattice distortion is essentially an isotropic expansion or contraction, whose magnitude tends to be proportional to the inverse of the particle size. Just as in a liquid drop, we find for spherical particles that[3]

$$\Delta a/a_0 = \tfrac{4}{3}\beta\gamma/D, \tag{5}$$

where β is the compressibility of the crystallite lattice, γ is the surface tension, and D is the particle diameter.

The effects of surfaces on the lattice structure could be considered in two ways.[1] For thin films the lattice distortions are generally thought to be confined to the outermost surface layers.[12] For microcrystals on the other hand, the lattice distortion can be considered to be essentially homogeneous throughout the whole microcrystal volume.[6] For this latter case, assuming some realistic crystalline potentials, Lennard-Jones[11] found that the average lattice spacing for ionic crystallites should be smaller, and that for covalent crystallites should be larger, than bulk. Such contractions have been observed by Boswell[2] in the ionic alkali halides, for example. Expansions in microcrystal lattices have been observed in microcrystals of the somewhat covalent compounds α-Fe_2O_3 [6,16,17] and MgO.[5] In all of these cases the lattice distortions appear to be roughly proportional to the inverse of the particle size. In this paper such lattice changes will be called *internal pressures*, where a positive internal pressure means that the lattice in the microcrystals has contracted as compared to bulk, and a negative internal pressure refers to a lattice expansion in the microcrystals. Orders of magnitudes

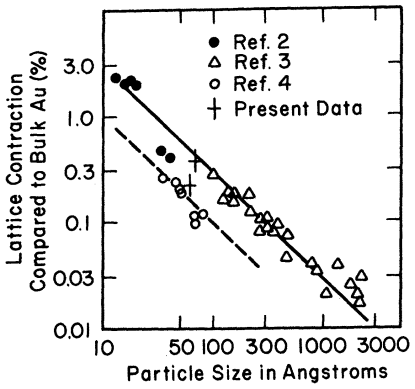

FIG. 4. Lattice spacing in gold microcrystals as a function of particle size. The data in Refs. 2–4 are for microcrystals produced by evaporation and are fitted, respectively, with a surface free energy of 3660 (solid line) and 1175 (dashed line) erg/cm^2. The crosses are the present data.

for these cases are as follows: In 50-Å NaBr microcrystals,[2] the contraction is equivalent to +2 kbar; in 50-Å α-Fe_2O_3 microcrystals,[6] the lattice expansion is equivalent to an internal pressure of −200 kbar.

Lattice contractions in gold microcrystals comparable to those measured in our samples have been observed previously. Boswell,[2] Mays *et al.*,[3] and Karioris *et al.*[4] produced gold microcrystals by evaporation techniques. Figure 4 shows the lattice contractions as a function of the particle size for these earlier experiments, together with our present experimental values. The microcrystals show consistently smaller lattice spacings than the bulk. However, the scatter in the results is quite extensive, with different preparation techniques leading to widely differing values of the surface tension. If we use Eq. 5 to extract values for the apparent surface tension γ_{Au} from these data, we see that a value of $\gamma_{Au}=3660$ ($\pm 30\%$) dyn/cm (solid line in Fig. 4) fits the data of Boswell[2] and Karioris *et al.*,[3] while the data of Mays *et al.*[4] can be fitted by $\gamma_{Au}=1175\pm 200$ dyn/cm (dotted line in Fig. 4). The values of the surface tension determined for our two samples fall between these two extremes, namely, at $\gamma_{Au}=1560\pm 430$ and 3120 ± 800 dyn/cm for our microcrystal samples I and II, respectively. In this evaluation we have taken the compressibility from the *International Critical Tables*[18] as $\beta=5.99\times 10^{-13}$ cm^2/dyn.

The experimental values for the surface tension of gold near the melting point, which might have been expected to be approximately comparable to the microcrystal values, are found to be typically about 1500 dyn/cm,[19–21] comparable to the Mays *et al.* data[4] and to our sample I.

There are clearly large discrepancies in the value for the surface tension not only among the various evaporation-technique values, but between the liquid-surface-tension value and our experimental data as well. It is clear that only the general trend and the order of magnitude of the lattice contractions can be generally predicted. More precise values of $\Delta a/a_0$ for any given sample must be obtained by direct measurements on *that* particular sample. These discrepancies are probably related to defects introduced in the preparation processes. For microcrystals of nonstoichiometric oxides, some of the observed lattice distortions have been associated with the defects created by excess oxygen diffusing into the lattice.[16,17,22]

These lattice contractions in gold microcrystals can be expressed in terms of internal pressures through the expression[8]

$$\Delta V/V_0=3\Delta a/a_0=-[5.547\times 10^{-4}P-7.72\times 10^{-7}P^2], \tag{6}$$

where P is the pressure in kbar, and $\Delta V/V_0$ is the volumetric contraction under pressure P. We then find internal pressures of $P=11.5$ and 19.3 kbar, respectively, for our samples I and II.

B. Mössbauer Isomer Shift versus Internal Pressure

In Fig. 5 we have plotted the Mössbauer isomer shift for our samples I and II as a function of the lattice contractions observed at room temperature. At the top of the graph are indicated the equivalent internal pressures in these microcrystals. If we assume the relative lattice contractions in the microcrystals at 4.2°K to be the same as at room temperature, then from Eq. (6) the Mössbauer isomer shift for both the microcrystals and the high-pressure work of Roberts *et al.*[8]

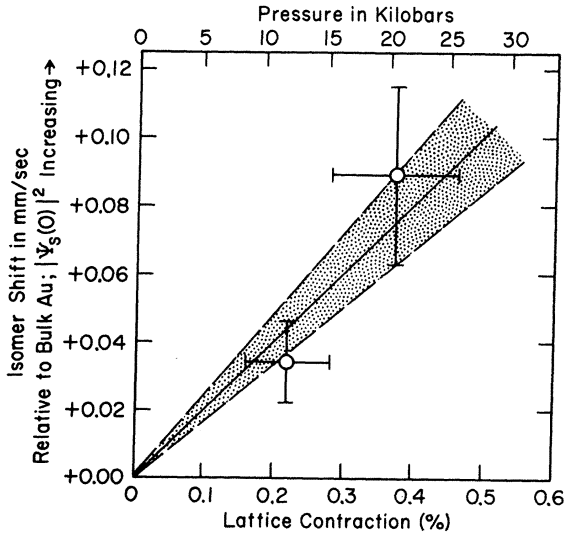

FIG. 5. Mössbauer isomer shift in gold microcrystals compared to the bulk value, plotted as a function of the lattice spacing. The solid line and shaded area are the experimental isomer shift versus pressure curve obtained by Roberts *et al.*, Ref. 8.

can be written in terms of the pressure as

$$v(P) = -g\Delta V/V_0 = g[5.547\times10^{-4}P - 7.72\times10^{-7}P^2]. \quad (7)$$

The heavy line and shaded area in Fig. 5 is a plot of Eq. (7) with $g=6.8\pm1$ mm/sec, as obtained experimentally by Roberts *et al.*[8] from their gold high-pressure measurements, and theoretically by Tucker *et al.*[7] through Wigner-Seitz calculations. A least-squares fit to our data gives a value of $g=6.2\pm2.3$ mm/sec. The agreement of this g with the high-pressure value reflects of course the satisfactory overlap of our experimental points with the shaded area in Fig. 5. Within the precision of both the isomer-shift data and the lattice-contraction measurements, the agreement is quite satisfactory.

IV. CONCLUSIONS

In these experiments we have seen for the first time a consistent Mössbauer isomer shift in any kind of microcrystals and we are able to explain it in terms of the internal pressure created in these microcrystals through surface tension and through defects. In the conclusions that we draw from these experiments, we emphasize the fact that it does seem to make sense to talk about an internal pressure in these microcrystals.

In a way, this relationship between external-pressure effects and these (ultimately very complex) surface phenomena seems too simplistic. However, in some earlier Mössbauer experiments on microcrystals, there were observed other effects, due to these lattice modifications, which could also be explained by this simple relationship. In α-Fe_2O_3 microcrystals, for example, the quadrupole interaction increases in the same amount for the negative internal pressures as it increases for equivalent thermal lattice expansions.[23] The Morin transition temperature in those microcrystals decreases under these negative internal pressures by the same amount as it increases under externally applied pressures.[6] There have been observed changes in Debye-Waller f factors by means of the ME in microcrystals of gold,[24] α-Fe_2O_3,[25] tin,[26] and tungsten,[27] and in several non-Mössbauer studies.[28–30] In the case of the gold microcrystals there were observed two separate effects on the recoilless fraction f. One change in f was induced by surface-mode phonons and by a low-frequency (long-wavelength) cutoff in the phonon spectrum due to the limited size of the microcrystals. The second change in f was due to an increase in the Debye temperature Θ_D. It has been suggested[31] that this increase in Θ_D was related to the lattice contractions in these microcrystals through the Grueneisen constant γ:

$$\Delta\Theta_D = \Theta_D[1-\gamma(\Delta V/V)]. \quad (8)$$

From an extrapolation of the microcrystal lattice-contraction data of Boswell,[2] an increase in Θ_D of (8 ± 2) °K was predicted between 200 and 60 Å gold microcrystals—compared to an observed value of (10 ± 2) °K. From our present measurements it is clear that such specific comparisons require the actual measurement of the lattice spacing for each sample in question; however, the sign and order of magnitude of the Θ_D increase are in agreement with the lattice contractions typically observed.

The major effects which might be expected to cloud our interpretation of the Mössbauer isomer shifts in these microcrystals are the modifications of electron densities by defects in the lattice. There are two types of defects possible in these microcrystals. First there may be internal defects, such as vacancies, spread throughout the microcrystal volume. Second, the microcrystal surface itself is one huge defect. If we assume that such internal defects are responsible for some of the variation in lattice spacing which occur between our samples I and II, then we can even estimate that their concentrations may be as much as parts per thousand. These internal defects will act somewhat like impurity atoms and, by acting as scattering centers for the conduction electrons,[32] will modify electron densities at neighboring gold nuclei and hence change the ME isomer shift. Similarly, the surface as a defect will present a scattering potential to the conduction electrons and hence may also modify the ME isomer shift. From the agreement of our present isomer-shift data with that from the high-pressure experiment with bulk gold,[8] it appears that either these effects are negligible, or at least cancel out, to within the accuracy of our measurements.

These results confirm the idea that the lattice-spacing variations in microcrystals can be considered to be equivalent to an externally applied pressure. This means that we might be able to investigate a variety of pressure effects without the use of high-pressure devices simply by preparing microcrystals of such samples. There are inherent limitations in such techniques. These include the difficulty of preparing such samples, the imprecision in determinations of the lattice contractions, and the intrinsically large distributions in particle size. However, there is no large-scale pressure apparatus necessary when using microcrystals and thus, particularly for low-temperature experiments and for low-energy γ rays, this technique offers certain advantages and certainly can be useful for exploratory work.

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Proposed Absolute Temperature Scale for Cerium Magnesium Nitrate below 0.003 K*

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The absolute temperature scale for single-crystal cerium magnesium nitrate (CMN) has been extended to entropies as low as $S/R=0.002$ by adiabatic demagnetization from values of H/T up to 68 kOe/K. The temperature dependence of the highly anisotropic angular distribution of the 255-keV γ ray from oriented ^{137m}Ce in the CMN provided the thermometric parameter. The nuclear-orientation results were interpreted with the spin Hamiltonian $\mathcal{H}=g_\perp\beta H_x S_x+B(S_xI_x+S_yI_y)$, where H_x is a calculated dipolar field. The hyperfine-structure constant B was determined by normalizing the higher-temperature nuclear-orientation results to the calorimetric results of Hudson and Kaeser and of Mess *et al.* at high entropies. A provisional temperature scale, based on both our nuclear-orientation results and the calorimetric work, is proposed. This scale is compared in detail with the results from earlier studies of CMN. The ^{137m}Ce γ-ray thermometer was also used to investigate the thermal behavior of cerium zinc nitrate (CZN). The preliminary nuclear-orientation results indicate a high degree of similarity between CZN and CMN.

I. INTRODUCTION

Cerium magnesium nitrate, $Ce_2Mg_3(NO_3)_{12}\cdot 24H_2O$ (CMN), has long been recognized as a substance capable of being cooled by adiabatic demagnetization to extremely low temperatures. The pioneer investigation of the temperature scale for single-crystal CMN was reported by Daniels and Robinson[1] in 1953. Using calorimetric methods, they found that the minimum temperature reached was 3.08 mK (millidegrees K) and was constant for all values of the magnetic entropy in the range $S/R\leq 0.45$. Above 6 mK Curie's law was found to be obeyed, with T and S related by $\ln 2-S/R=3.2\times 10^{-6}T^{-2}$. In a subsequent reanalysis of their data, de Klerk[2] asserted that the temperature did not become constant at $S/R=0.45$ but continued to decrease to 2.25 mK at $S/R=0.150$.

In 1965 Frankel, Shirley, and Stone[3] demonstrated that nuclear orientation could be used to determine the temperature scale of CMN. They found that both of the above T-S relations were unable to explain the